

DT 2,252,186

Job N .: 1505-93180

Ref.: DE 2552186

Translated from German by the Ralph McElroy Translation Company
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FEDERAL REPUBLIC OF GERMANY
 GERMAN PATENT OFFICE
 PATENT NO. 2 252 186
 (Offenlegungsschrift)

Int. Cl. : C 07 c, 43/30
 C 08 g, 23/02
 C 11 d, 1/72

German Cl.: 12 o, 5/09
 39 b5, 23/02
 23 e, 2

Filing No.: P 22 52 186.5

Filing Date: October 25, 1972

Publication Date: May 16, 1974

ALKALI-RESISTANT, SURFACE-ACTIVE FOAM-SUPPRESSING AGENTS (ACETALS)

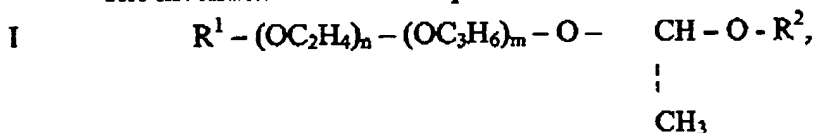
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The invention concerns compounds of formula I



in which R^1 means a straight chain or branched saturated or unsaturated alkyl residue with 7 to 22 carbon atoms or a mono- or binuclear alkylaryl residue with 8 to 12 carbon atoms in the alkyl chain, R^2 means a straight chain or branched alkyl residue with 1 to 10 carbon atoms, an optionally alkyl-substituted cyclohexyl residue or a residue of the formula $(\text{C}_3\text{H}_6\text{O})_m - (\text{C}_2\text{H}_4\text{O})_n$

— R^1 , n means a whole number from 1 to 30, and m means a whole number from 5 to 50, with the stipulation that the ratio of m to n is at least 1:1.

Although polyalkoxylated phenols and polyalkoxylated aliphatic alcohols are suitable nonionic surfactants, they are not suitable for use in industrial cleaning formulations, since the presence of alkaline substances is necessary in these formulations. Polyalkoxylated aliphatic alcohols or alkylphenols are easily degraded by oxidation in the presence of strongly alkaline compounds like caustic alkali or soda, which leads to decompositions and discolorations.

It is now known that the free terminal hydroxyl groups of polyalkoxylated alcohols or phenols can be reacted with reactive groups to achieve stable polyethers. This teaching is the object of the German Patent Application [Offenlegungsschrift] 1 520 647, where polyethoxylated alcohols or alkylphenols are reacted with olefins so that the end groups, i.e., the free hydroxyl groups, become closed.

Symmetric end group-closed polyglycol ethers that were obtained by the two-sided reaction of polyglycol ethers based on ethylene oxide with higher vinyl ethers, are described in the American Patent 2 905 721. These compounds are designated as raw materials for good low-foaming cleaning agents in this literature citation.

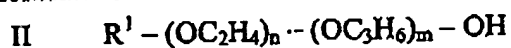
In spite of the very good wetting properties of these products the foam suppression of these agents still leaves more to be desired. In automatic dishwashing machines too little water reaches the surfaces to be cleaned and the mechanical support of the washing action by the moving parts of the machine is inhibited if washing agent formulations that are too highly foaming are used.

It is known that, besides compounds like ethers, etc., acetals and ketals are extremely resistant to alkalis. If vinyl ethers are added to the known polyalkoxylated alcohols or alkylphenols mentioned above, then under quite specific circumstances one will obtain mixed and symmetric acetals of these polyalkoxylated alcohols or phenols.

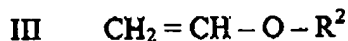
The compounds of formula I have now surprisingly turned out to be excellent alkali-stable surfactants with considerably better foam-suppressing properties while having the same good washing power and biodegradability.

The excellent foam-suppressing action of the compounds in accordance with the invention is achieved not lastly through the ratio of propylene oxide to ethylene oxide of at least 1:1, whereas in accordance with previous patent a higher fraction of ethylene oxide compared to propylene oxide (ratio at least 3:2) was always sought in the case of such alkoxyates in order to leave a sufficiently high fraction of hydrophilic groups in the molecule.

The preparation of the new acetals of formula I is simple and is carried out by reacting a polyalkoxylated alcohol of formula II



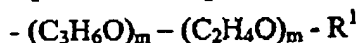
with a vinyl ether of formula III



in the presence of acid catalysts. In formulas II and III R^1 , R^2 , n and m have the same meanings as in formula I.

Lewis acids like BF_3 , AlCl_3 , TiCl_4 or mineral acids like HCl , H_3PO_4 , H_2SO_4 or HClO_4 are especially suitable as catalysts. Strong organic acids like methanesulfonic acid, propanesulfonic acid, trinitrobenzenesulfonic acid, *p*-toluenesulfonic acid, trifluoromethanesulfonic or trifluoroacetic acid also catalyze the reaction of the polyalkoxylated alcohols or phenols with vinyl ethers very well.

The reaction can expediently be carried out at temperatures from 0 to 100°C. If temperatures < 30°C are chosen, in general compounds of formula I in which R^2 stands for alkyl residues or cycloalkyl residues of the above description generally result, whereas at temperatures above 30°C and with increasing temperatures compounds in which R^2 stands for the residue



in general arise. If one desires compounds with a low cloud point, the reaction is expediently carried out at the higher temperatures.

However, the reaction is preferably carried out at the lower temperatures, since the best compounds from the standpoint of application technology result from this.

Long chain alcohols with 7 to 22 carbon atoms are possibilities as starting materials. They can be saturated or unsaturated and unbranched or branched and include all alcohols with the said number of carbons or their mixtures. Preferably, alcohol mixtures as are obtained from Ziegler or cracking olefins by oxosynthesis are used. Especially preferred alcohol fractions are, for example, the C_{12} - C_{15} or C_{14} - C_{16} cuts.

Other starting products are the known isomer alkylphenols or alkylnaphthols, where the alkyl residues contain 8 to 12 carbon atoms. Here starting materials like octylphenol or nonylphenol are of particular importance within the scope of the invention.

The said substances, preferably the C_9 to C_{16} alcohol fractions, are first reacted with 1 to 30 mol, preferably 5 to 20 mol ethylene oxide and then propoxylated, using propylene oxide in an amount so that the mol ratio of propylene oxide to ethylene oxide is at least 1:1, preferably however 1.1:1 up to 6:1. one expediently uses 5 to 50 mol propylene oxide, preferably 10 to 25 mol.

The ethoxylation or subsequent propoxylation takes place by well known methods in the presence of alkali catalysts like KOH or NaOH , where the addition of ethylene oxide takes place at temperatures of, for example, 130 to 160°C and pressures from 0 to 5 atm (gage) and the propoxylation takes place, for example, at pressure of 110 to 130°C and pressures of 0 to 10 atm (gage).

Then the polyalkoxylated alcohols or phenols of the above definition are reacted with a vinyl ether of formula III to form compounds of formula I using small amounts of strong inorganic or organic acid or Lewis acids as catalysts. To make the reaction go as quantitatively as possible, one expediently uses 2 to 3 mol of the vinyl ether of formula III per free hydroxyl group.

In formula I and III R^2 is preferably an alkyl residue with 1 to 10 carbon atoms or an optionally alkyl-substituted cyclohexyl residue, where 2-methyl and 2-ethyl residues especially are possibilities as alkyl substituents. Preferred vinyl ethers of formula III that can be used to produce the compounds of formula I in the sense in accordance with the invention are, for example, methyl vinyl ether, ethyl vinyl ether, isopropyl vinyl ether, n-butyl and isobutyl vinyl ethers as well as 2-methylcyclohexyl vinyl ether.

The addition of the vinyl ether should take place at the temperatures indicated above.

The compounds in accordance with the invention are excellently suitable as formulations with solid sodium hydroxide or sodium metasilicate and tripolyphosphate, among other things, as low-foaming, alkali-stable industrial cleaning agents for solid surfaces of all kinds, for example as metal cleaners before plating, preparation and processing and also as cleaners in automatic dishwashing and bottle washing machines. Washing agent formulations of this kind contain, for example, in addition to 2 to 5 parts of the new surfactants, 75 parts solid sodium hydroxide and 25 parts sodium metasilicate or in addition to 50 parts sodium hydroxide per 25 parts sodium tripolyphosphate and sodium metasilicates as detergent fillers.

Even with lengthy standing no discoloration and degradation occurs with these formulations, which can easily be observed from the poorer foaming behavior.

The substances in accordance with the invention are, however, also suitable in other mixtures as wetting or cleaning agents for the treatment of textiles and the cleaning of nonporous surfaces of all kinds.

The resulting products proved to be excellently effective cleaning agent surfactants with good surface activity and boundary activity, with low foaming behavior. The simultaneous very good alkali stability was shown in the good color stability in contact with strong alkali at normal and elevated temperatures over long periods of time. Under these chemical and thermal stresses the boundary-active functions in the form of surface tension, wetting action and low foaming quality proved to be practically unchanged.

The following examples illustrate the invention with regard to the preparation of the compounds and their use as cleaning agents for solid surfaces. The parts and percents indicated there refer to weight.

Example 1

3 to 4 parts of a 5 to 10% solution of boron trifluoride etherate in diethyl ether is added by drops to a mixture of 400 parts of reaction product of a C_{12} - C_{15} oxo alcohol mixture with 5 mol ethylene oxide and 15 mol propylene oxide and 72 parts ethyl vinyl ether that has been cooled to about 10°C. The reaction mixture is kept at 5 to 15°C by additional cooling while stirring. After 2 to 3 hours the temperature is slowly allowed to rise to room temperature and the mixture is then stirred for another 1 to 2 hours.

The catalyst is then removed by stirring with 2 parts sodium carbonate for 30 minutes. After filtration the excess ethyl vinyl ether, acetaldehyde diethylacetal that possibly resulted, and other volatile components are removed in a vacuum under mild heating to about 40°C while stirring. One obtains a water-clear pale product in a 96 to 99% yield.

The resulting surfactant, a mixture of symmetric and asymmetric acetal of acetaldehyde with polyalkoxylated C_{12} - C_{15} oxo alcohol and ethanol, is extremely low foaming and has very good wetting properties while having extreme alkali stability (see table).

The compounds listed below in Table I were compared similarly and subsequently tested for industrial application properties.

3 different samples were used to test the alkali stability in order to evaluate the behavior under different conditions:

Experiment 1

In a flat porcelain dish about 15 cm in diameter 45.00 g sodium metasilicate pentahydrate is spread out in a thin even layer. The dish is placed on a laboratory scale with a precision of 0.01 g. Then 5.00 g of the surfactant to be tested is sprayed as uniformly as possible onto the surface of the powder using a spray device. Then substances are very thoroughly mixed with a spatula without loss of substance again after being quantitatively transferred to a mortar and thoroughly ground with the pestle in order to achieve a high degree of homogeneity of the mixture.

An aliquot part precisely measured by weight is taken from this mixture, for example half, weighed out into a 10 cm diameter Petri dish and evenly spread there in a thin layer. This fraction is called portion A and is stored for 40 days at 60°C in a heating chamber in a normal atmosphere. Every 3 to 5 days the sample is removed and visually checked for color changes. The aliquot residue of the total mixture, which is called portion B, is used to measure the initial value of the surface tension (10 g/L distilled water, 20°C, Lecomte de Nouy tensiometer), for the initial measurement of the following volume in accordance with DIN 53 902, Sheet 1 (25°C, 20 g/L distilled water) and for the storage sample at room temperature in a normal laboratory

atmosphere in order to test for color stability (40 days storage time). Visual evaluation of any possible color changes takes place in the same way as with portion A (see above).

The end samples for tests regarding surface tension and foam volume are taken from portion A after 40 days. Now it is first necessary to precisely establish the current weight of portion A so that the aliquot weight fraction that corresponded to 1.00 g at the beginning of the storage time, if, for example, 100 g of a 10 g/L solution is supposed to be made, can be taken for the surface tension measurement. The same is valid for the preparation of the 20 g/L solution for foam testing.

Experiment 2

50 g 50% sodium hydroxide is intensively mixed in a beaker with 0.5 g of the surfactant to be tested and then transferred to a test tube. This is held in a heating chamber at 60°C for 50 days without being sealed. The surfactant separates as a separate layer on the liquid surface in the heat. Observations are made of the change of color both in the upper organic phase and the lower aqueous alkaline phase at uniform periods of time of 3 to 5 days.

Experiment 3

10 g sodium hydroxide pellets poured into a test tube containing 20 g surfactant at room temperature. The mixture is left open at room temperature in the normal laboratory atmosphere for 12 days. Observations are made of color changes both in the upper organic liquid and in the boundary layer of the sodium hydroxide pellets at equal time intervals, for example every 2 days.

No changes of color were observed even after week of standing in all 3 experiments for the products in accordance with Examples 2, 3, 5 to 13, 15, 17 and 18.

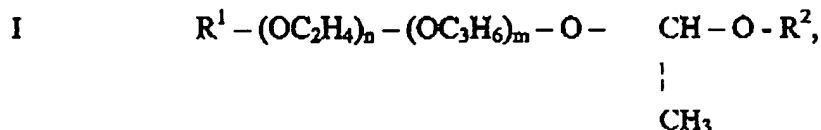
The products in accordance with Examples 4, 14 and 16 begin to turn yellow after only 2 to 3 days, and the color change became stronger with increasing time.

Table

Example	Starting compound	Mol (C ₂ H ₄ O)	Mol (C ₆ H ₆ O) R ²	Cloud point (1% in 40% butyl glycol)	Surface tension (dyne·cm ⁻¹)	Foam behavior (IG impact method)			
						1 min	5 min	10 min	
2	C ₇ -C ₁₁ -Oxo alcohol	5	6 C ₂ H ₅	46.5	29.5	100	70	30	
3	C ₇ -C ₁₁ -Oxo alcohol	5	13 i-C ₄ H ₉	44.5	29.8	100	50	20	
4	C ₁₂ -C ₁₅ -Oxo alcohol	5	0 i-C ₄ H ₉	59.6 (in H ₂ O)	24.9	480	100	70	
5	" " "	5	6 CH ₃	45.9	30.1	50	20	5	
6	" " "	5	6 C ₂ H ₅	46.3	30.9	9	5	0	
7	" " "	5	6 i-C ₄ H ₉	43.7	30.4	10	5	0	
8	" " "	5	13 CH ₃	46.4	30.5	0	0	0	
9	" " "	5	13 C ₂ H ₅	49.9	31.4	10	8	0	

Claims

1. Compounds of the formula I



in which R^1 means a straight chain or branched saturated or unsaturated alkyl residue with 7 to 22 carbon atoms and a mono- or binuclear alkylaryl residue with 8 to 12 carbon atoms in the alkyl chain, R^2 means a straight chain or branched alkyl residue with 1 to 10 carbon atoms, and optionally alky substituted cyclohexyl residue or residue of the formula $(\text{C}_3\text{H}_6\text{O})_m - (\text{C}_2\text{H}_4\text{O})_n - \text{R}^1$, n means a whole number from 1 to 30 and m means a whole number from 5 to 50, with the stipulation that the ratio of m to n is at least 1:1.

2. Industrial cleaning agents or washing agents containing at least one compound in accordance with Claim 1.